

Theory of photoinduced charge transfer in weakly coupled donor-acceptor conjugated polymers: application to an MEH-PPV:CN-PPV pair

M. W. Wu and E. M. Conwell

*Center for Photoinduced Charge Transfer, Chemistry Department, University of Rochester,
Rochester, New York 14627, USA
and Xerox Corporation, Wilson Center for Technology, 114-22D, Webster, New York 14580,
USA**

Abstract

In a pair of coupled donor-acceptor conjugated polymer chains, it is possible for an exciton photoexcited on either polymer to decay into a hole in the donor polymer's valence band and an electron in the conduction band of the acceptor polymer. We calculate the corresponding exciton decay rate and its dependence on inter-polymer distance. For a pair of derivatives of poly(phenylene vinylene), PPV, specifically poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-1, 4 PPV], MEH-PPV, and poly(2,5-hexyloxy *p*-phenylene cyanovinylene), CN-PPV, at a separation of 6 Å the characteristic decay time is 2.2 ps, whereas at 4 Å it is ~ 50 fs.

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I. INTRODUCTION

It was found recently that photoconductivity can sometimes be greatly enhanced by doping derivatives of poly(phenylene vinylene), PPV,¹ poly(thiophene)² and the σ -conjugated polymer poly(methylphenylsilylene)³ with the fullerene molecule C₆₀. This led to construction of photovoltaic cells containing a polymer-fullerene heterojunction.⁴⁻⁷ However these devices had poor efficiency because few of the photogenerated carriers were able to reach the electrodes. Recently a great increase in efficiency was obtained by the use of interpenetrating donor (D) and Acceptor (A) networks so that D-A junctions are distributed throughout the device.^{8,9} In one embodiment D is MEH-PPV and A is CN-PPV.⁸ Because of the cyano side groups on the PPV chains, the electron affinity of CN-PPV is greater than that of MEH-PPV while the ionization potential of MEH-PPV is less than that of CN-PPV. Therefore electrons in the excitons photoexcited on MEH-PPV chains will tend to move onto CN-PPV chains while holes in the excitons on CN-PPV chains tend to move onto MEH-PPV.

Recently, Rice and Gartstein¹⁰ developed a microscopic theory of the photogeneration process to calculate the rate of photoinduced charge transfer due to exciton dissociation between a polymer chain and an adjacent acceptor molecule. An essential feature of this theory is that the transfer occurs with energy being conserved, *i.e.*, no phonons are involved. They simplified their theory by neglecting the effects of lattice relaxation, *i.e.*, polaron formation. Rice and Gartstein suggested that their theory could be generalized to the case of the acceptor being another chain rather than a molecule. In this paper we carry out such a generalization to study the dissociation of an exciton photoexcited on either the donor or acceptor chain into a free hole in the donor polymer's valence band and an electron in the conduction band of the acceptor polymer. The theory is applied to an MEH-PPV:CN-PPV pair. We have extended it to investigate the dependence of the dissociation rate on the distance between D and A.

II. MODEL

We start our discussion from a model Hamiltonian for two coupled conjugated polymer chains of infinite length, $H = H_0 + H_1 + H_2$. H_0 describes the intrachain and charge-transfer (CT) electron-hole (e-h) pair excitations of the two polymer chains considered independent. By the term intrachain e-h excitations we refer to the excitations of one chain without regard to the presence of the other polymer chain, while by CT e-h excitation we mean the excitation of a charge on one polymer chain in the presence of a charge of opposite sign on the adjacent chain. Such excitations have also been called interchain excitons, indirect excitons and polaron pairs. H_0 includes no coupling between the two chains except for the long-range Coulomb interaction between electron and hole. H_1 and H_2 represent the coupling between the two chains, taken to be weak perturbations that cause the interchain charge transfer. The former describes single-particle hopping and the latter a process in which a charge fluctuation in one species scatters a charge of the other species from one polymer chain to the other.¹⁰

It is convenient to assume that each polymer chain has e-h symmetry and measure energies from the center of its gap. Because the gap centers of the two polymers need not

coincide, we will take our zero of energy at the gap center of the second polymer, that of the first polymer differing from this by the energy $\pm\Delta$. H_0 may then be written

$$\begin{aligned}
H_0 = & \sum_{n\sigma} [(\alpha_0 \mp \Delta) a_{n\sigma}^\dagger a_{n\sigma} + (\alpha_0 \pm \Delta) b_{n\sigma}^\dagger b_{n\sigma} - t(a_{n+1\sigma}^\dagger a_{n\sigma} + \text{H.C.}) \\
& - t(b_{n+1\sigma}^\dagger b_{n\sigma} + \text{H.C.})] - \sum_{mn\sigma s} U(n-m) b_{n\sigma}^\dagger b_{n\sigma} a_{ms}^\dagger a_{ms} \\
& + \sum_{n\sigma} [\bar{\alpha}_0 (c_{n\sigma}^\dagger c_{n\sigma} + d_{n\sigma}^\dagger d_{n\sigma}) - \bar{t}(c_{n+1\sigma}^\dagger c_{n\sigma} + \text{H.C.}) \\
& - \bar{t}(d_{n+1\sigma}^\dagger d_{n\sigma} + \text{H.C.})] - \sum_{mn\sigma s} \bar{U}(n-m) d_{n\sigma}^\dagger d_{n\sigma} c_{ms}^\dagger c_{ms} \\
& - \sum_{mn\sigma s} V_1(n-m) d_{n\sigma}^\dagger d_{n\sigma} a_{ms}^\dagger a_{ms} - \sum_{mn\sigma s} V_2(n-m) b_{n\sigma}^\dagger b_{n\sigma} c_{ms}^\dagger c_{ms} , \tag{1}
\end{aligned}$$

where $b_{n\sigma}^\dagger$ ($d_{n\sigma}^\dagger$) and $a_{n\sigma}^\dagger$ ($c_{n\sigma}^\dagger$) create an electron in the conduction band and a hole in the valence band, respectively, located at the n th monomer with spin σ in the first (second) chain. α_0 ($\bar{\alpha}_0$) denotes the center of each band measured from midgap. The upper (lower) sign before Δ refers to the case where the midgap is above (below) the zero of energy. From the first and third terms, one can easily get the single electron and single hole energy spectra: $\varepsilon_{ke} = \alpha_0 \pm \Delta - 2t \cos(ka)$ and $\varepsilon_{kh} = \alpha_0 \mp \Delta - 2t \cos(ka)$ of the first chain and $\bar{\varepsilon}_{ke} = \bar{\varepsilon}_{kh} = \bar{\alpha}_0 - 2\bar{t} \cos(k\bar{a})$ of the second chain. Accordingly in these expressions $W = 4t$ ($\bar{W} = 4\bar{t}$) is the band width. a (\bar{a}) represents the length of a monomer of the first (second) polymer chain. From the excitation spectrum, one can easily get the energy gaps of e-h excitation, *ie.*, the minimum energy required to create an e-h pair in one polymer chain, $E_g = 2(\alpha_0 - 2t)$ of the first chain and $\bar{E}_g = 2(\bar{\alpha}_0 - 2\bar{t})$ of the second chain. It is then straightforward to see that one should assume $\alpha_0 > 2t$ and $\bar{\alpha}_0 > 2\bar{t}$ in order to have E_g (\bar{E}_g) > 0 . The second and fourth terms in Eq. (1) represent the intrachain Coulomb interaction with

$$\bar{U}(n-m) = \bar{U} \delta_{nm} + \frac{\bar{V}}{|n-m|} (1 - \delta_{nm}) , \tag{2}$$

for the second chain and the corresponding expression for the first chain with \bar{U} and \bar{V} replaced by U and V . The last two terms of Eq. (1) denote the interchain Coulomb interactions. For simplicity, we assume $V_1(n-m)$ equals $V_2(n-m)$, with

$$V_1(n-m) = V_2(n-m) \equiv V(n-m) = \frac{V_1}{\sqrt{(n-m)^2 + B}} , \tag{3}$$

where $B = \kappa_{\parallel} d^2 / (\kappa_{\perp} a^2)$ and d stands for the perpendicular distance between the two chains.¹¹ κ_{\parallel} and κ_{\perp} are dielectric constants along and perpendicular to the polymer chains, respectively.

The Hamiltonian

$$H_1 = t'_{\perp} \sum_{n\sigma} (d_{n\sigma}^\dagger b_{n\sigma} + \text{H.C.}) + t''_{\perp} \sum_{n\sigma} (c_{n\sigma}^\dagger a_{n\sigma} + \text{H.C.}) \tag{4}$$

represents the perturbation leading to the single-particle interchain hopping process with t'_{\perp} and t''_{\perp} being electronic hopping integrals. In general, t'_{\perp} and t''_{\perp} are not necessarily the same. It is reasonable to assume they fall off exponentially according to¹²

$$t'_\perp = t'_0 e^{-\mu d} = t'_0 \exp(-\mu a \sqrt{B\kappa_\perp/\kappa_\parallel}) , \quad \text{and} \quad t''_\perp = t''_0 e^{-\mu d} = t''_0 \exp(-\mu a \sqrt{B\kappa_\perp/\kappa_\parallel}) . \quad (5)$$

The charge-fluctuation transfer process is described by

$$H_2 = \sum_{mn\sigma s} v_1(n-m)(b_{n\sigma}^\dagger c_{ms}^\dagger c_{ms} d_{n\sigma} + \text{H.C.}) + \sum_{mn\sigma s} v_2(n-m)(a_{n\sigma}^\dagger d_{ms}^\dagger d_{ms} c_{n\sigma} + \text{H.C.}) , \quad (6)$$

where the first term corresponds to an electron being scattered to the other chain by a local fluctuation of the hole density in the vicinity of site m , and in the second term the roles of electron and hole are reversed. We further assume that the matrix element $v_{1(2)}(n-m) = \tilde{v}_{1(2)}/\sqrt{(n-m)^2 + B}$, because, like $V_1(n-m)$ and $V_2(n-m)$, it depends on the Coulomb attraction between the electron and hole on separate chains. It is noted that $\tilde{v}_{1(2)}$ is also related to the electron hopping integrals and would vanish if t'_\perp (t''_\perp) = 0. Therefore, we further assume $\tilde{v}_{1(2)} = v_{1(2)}e^{-\mu d}$. However, we stress here that v_1 (v_2) may also have additional dependence on B . Again, v_1 is not necessarily equal to v_2 .

In the following discussion of charge transfer, we always assume that the exciton is photogenerated on the second chain. The exciton can dissociate either with transfer of an electron or a hole to the first chain as shown schematically in Fig. 1. It can also be deduced from Fig. 1 that only for the midgap of the first chain above that of the second chain is it possible to have hole transfer (HT) without electron transfer, while only for the midgap of the first chain below that of the second chain is it possible to have electron transfer (ET) without hole transfer. Additionally, for both HT and ET, in order that the other carrier not hop to the other chain as well, it is necessary to satisfy the additional condition $\bar{E}_g < E_g + 2\Delta$.

We first discuss in detail the case of hole transfer. With the intrachain and interchain Coulomb interaction included, the intrachain e-h excitation spectrum of the second polymer chain consists of an intrachain exciton with energy $\bar{\omega}_0$ and a continuum band of width $2\bar{W}$ above the energy gap \bar{E}_g . The HT e-h excitation spectrum consists of an interchain (HT) exciton with energy ω_{HT} and a continuum band of width $\bar{W} + W$ above the gap $\bar{E}_g/2 + E_g/2 - \Delta$. (See Fig. 1). Energy conservation requires that CT due to an intrachain exciton in the second chain giving up a hole to the first chain (HT) can only take place when

$$\bar{E}_g/2 + E_g/2 - \Delta \leq \bar{\omega}_0 \leq \bar{E}_g/2 + E_g/2 - \Delta + \bar{W} + W . \quad (7)$$

The decay rate of the exciton can be written from the Fermi golden rule:

$$1/\tau = (2\pi/\hbar) \sum_{\alpha f} |M_{\alpha f}|^2 \delta(\omega_0 - \varepsilon_f) . \quad (8)$$

In this equation, $M_{\alpha f} = \langle f | H_\alpha | i \rangle$ ($\alpha = 1, 2$) is the matrix element describing the transition from the initial intrachain exciton state $|i\rangle$ to the final CT e-h excitation states.

The intrachain spectrum can be acquired as follows. We first construct a two-particle wave function of a singlet e-h pair excitation on the second polymer chain as

$$\bar{\Phi} = \frac{1}{\sqrt{2}} \sum_{nm\sigma} \bar{\Phi}_{nm} c_{n\sigma}^\dagger d_{m-\sigma}^\dagger |0\rangle , \quad (9)$$

with $|0\rangle$ denoting the ground state. $\bar{\Phi}_{nm}$ is assumed to be real and is normalized according to $\sum_{nm} \bar{\Phi}_{nm}^2 = 1$. From $H_0 \bar{\Phi} = E \bar{\Phi}$, we obtain for the lowest excitonic bound state with energy $\bar{\omega}_0$,¹⁰

$$(E - 2\bar{\alpha}_0)\bar{\Phi}_{n-m} = -2\bar{t}(\bar{\Phi}_{n-m+1} + \bar{\Phi}_{n-m-1}) - \bar{U}(n-m)\bar{\Phi}_{n-m} . \quad (10)$$

Similarly we can construct a two-particle HT wavefunction as

$$\Phi_{HT} = \frac{1}{\sqrt{2}} \sum_{nm\sigma} \phi_{nm} c_{n\sigma}^\dagger b_{m-\sigma}^\dagger |0\rangle . \quad (11)$$

ϕ_{nm} is given by the equation

$$[E - \bar{\alpha}_0 - (\alpha_0 - \Delta)]\phi_{n-m} = -(t + \bar{t})(\phi_{n-m+1} + \phi_{n-m-1}) - V(n-m)\phi_{n-m} , \quad (12)$$

with the normalization condition $\sum_n \phi_n^2 = 1/N$, where N is the number of monomers on the chain. (here we have assumed ϕ_n to be real). It is noted that in the above we only retain the solutions with zero CM wave vector, indicated by a superscript 0 on Φ and $\bar{\Phi}$, as is required for momentum conservation. Because we assume that free carriers are generated by the dissociation, we only need to get the scattering states of these equations in order to calculate $1/\tau$.

The decay rate of an exciton in the second chain by transferring a hole to the first chain may now be written as

$$1/\tau_\alpha = (2\pi/\hbar)(g_\alpha^2/\bar{E}_g)\Gamma_\alpha \quad (13)$$

with $\alpha = 1$ standing for the process of single-particle hopping and $\alpha = 2$ for the charge fluctuation process. We take $g_1 = t_0''$ and $g_2 = v_2$. The dimensionless rate Γ_α , which differs from that defined by Rice and Gartstein, is defined by

$$\Gamma_\alpha = \bar{E}_g \sum_\nu |M_\alpha(\nu)|^2 \delta(\bar{\omega}_0 - \varepsilon_\nu) , \quad (14)$$

where

$$M_1(\nu) = N \sum_n e^{-\mu a \sqrt{B\kappa_\perp/\kappa_\parallel}} \phi_n(\nu) \Phi_n^0 \quad (15)$$

$$M_2(\nu) = N \sum_n \frac{e^{-\mu a \sqrt{B\kappa_\perp/\kappa_\parallel}}}{\sqrt{n^2 + B}} \phi_n(\nu) \Phi_n^0 . \quad (16)$$

III. CALCULATIONS AND DISCUSSIONS

We apply our theory to an MEH-PPV:CN-PPV pair. We consider first an exciton photoinduced on the CN-PPV chain. This exciton is dissociated by transferring a hole to MEH-PPV. To this end, we take the second chain as CN-PPV and the first one as MEH-PPV. The values of the various unknown parameters in Eq. (10) (written with unbarred quantities for the first chain) must be chosen to give the correct gap and exciton binding energy. For MEH-PPV the optical absorption edge is at 2.1 eV.¹³ The single particle energy gap of MEH-PPV has been measured as 2.45 eV.¹⁴ The exciton binding energy is the difference of these two numbers,¹⁵ thus 0.35 eV. The intrachain Coulomb potential coefficient V or \bar{V} is of the order of the Coulomb attraction between an electron and a hole separated by one

monomer ($a = 6.5 \text{ \AA}$), which is $\sim 1/2 \text{ eV}$.¹⁰ $V \sim 0.42 \text{ eV}$. Choosing $\alpha_0 = 3.2 \text{ eV}$, $t = U = 1 \text{ eV}$,¹⁰ and $V = 0.44 \text{ eV}$, we obtain from Eq. (10) $E_g = 2.4 \text{ eV}$, the exciton creation energy $\omega_0 = 2.065 \text{ eV}$ and its binding energy $\epsilon_b = 0.335 \text{ eV}$. For CN-PPV the optical absorption edge is at $\sim 2.3 \text{ eV}$.¹⁶ It is reasonable to assume that the exciton binding energy is similar to that of PPV and MEH-PPV. With $\bar{\alpha}_0 = 3.3 \text{ eV}$, $\bar{t} = \bar{U} = 1 \text{ eV}$, and $\bar{V} = 0.4 \text{ eV}$, we obtain $\bar{E}_g = 2.6 \text{ eV}$, the exciton creation energy $\bar{\omega}_0 = 2.285 \text{ eV}$ and $\bar{\epsilon}_b = 0.315 \text{ eV}$.

To obtain numerical results for HT we further take $\kappa_{\parallel} = 8$,¹⁷ $\kappa_{\perp} = 3$, $V_1 = 0.44 \text{ eV}$, the energy difference between gap centers of MEH-PPV and CN-PPV $\Delta = 0.5 \text{ eV}$,⁸ and $\mu = 1.18 \text{ \AA}^{-1}$.¹² For the numerical calculations, we employ a chain of $N = 400$ unit cells for each of the polymers and use periodic boundary conditions. We then numerically solve Eq. (12) for the CT band eigenfunctions $\phi_n(\nu)$ and their eigenvalues ε_{ν} and substitute them and the numerical solution of Eq. (10) into Eq. (14) to get Γ_{α} . In evaluating Γ_{α} , we replace the δ -function in Eq. (14) by a Gaussian with variance $\sigma = 0.032 \text{ eV}$. The resulting Γ_{α} ($\alpha = 1, 2$) are plotted as solid curves as a function of B . Since B is proportional to the square of the distance between the chains, the transfer rate falls off very rapidly with increasing B . We estimate the minimum chain separation as $\sim 4 \text{ \AA}$, giving the minimum $B \sim 1$. An increase in interchain distance by a factor 2 is seen to decrease the transfer rate Γ_1 by almost 4 orders of magnitude, and Γ_2 even more.

Rewriting the first inequality in Eq. (7) we obtain the threshold value of Δ ,

$$\Delta_T = E_g/2 - \bar{E}_g/2 + \bar{\epsilon}_b. \quad (17)$$

For HT in this case Eq. (17) gives $\Delta_T = 0.2 \text{ eV}$. It is noteworthy that Γ_1 and Γ_2 peak at the threshold value of Δ . This was also found to be the case for the calculation of charge transfer to a dopant molecule.¹⁰ The appearance in Fig. 2 of finite Γ values below the threshold is due to the replacement of the δ -function in Eq. (14) by a Gaussian.

It is possible to change Δ by changing one or both of the polymers or by application of an electric field perpendicular to the chains. For an electric field of $5 \times 10^6 \text{ V/cm}$, for example, if the MEH-PPV and CN-PPV chains were separated by 4 \AA , the change in Δ due to the field would be $\pm 0.2 \text{ eV}$. Thus Δ for HT in MEH-PPV:CN-PPV would be either 0.3 or 0.7 eV depending on the direction of the electric field. As can be seen in Figs. 3(a) and 3(b), for Γ_1 this could be a change by a factor 2. For Γ_2 the change is smaller because Γ_2 decreases less rapidly with increase in Δ . Thus the dissociation rate may be substantially increased or decreased by high electric fields.

Having Γ_1 , we can get an approximate value, or at least an upper limit, for τ_1 using the average of t_0'' values for MEH-PPV and CN-PPV, the individual values having been determined from the energy shift between exciton and excimer emission.¹⁸ That average is $t_0'' = 24 \text{ eV}$. For a spacing of 6 \AA between MEH-PPV and CN-PPV $B = 2.25$, leading to $\Gamma_1 = 2 \times 10^{-7}$ for $\Delta = 0.5 \text{ eV}$ and $\tau_1 = 2.17 \text{ ps}$. For 4 \AA , $B = 1.00$ leading to $\tau_1 = 47.7 \text{ fs}$ for $\Delta = 0.5 \text{ eV}$. Thus the dissociation process we are calculating is quite rapid.

Consider now the case of an exciton photoinduced in MEH-PPV dissociating into an e-h pair by transferring an electron to CN-PPV. For this calculation we take the second chain to be MEH-PPV, thus interchanging \bar{E}_g , $\bar{\alpha}_0$, \bar{t} , \bar{U} and \bar{V} with E_g , α_0 , t , U and V respectively. Equations (7) and (12) derived for the HT case are unchanged. Numerical solution of the equations, as described earlier, leads to Γ_{α} for ET shown as the dashed curves in Fig. 2 and 3. The threshold value of Δ for ET determined from Eq. (17) is 0.4 eV rather than 0.2 eV

because of the interchange of E_g and \bar{E}_g ; the exciton is generated on the chain with the smaller gap in this case. Apart from the difference in threshold, Γ_α for ET varies with Δ and B in similar fashion to the case for HT. The decay rate $1/\tau_\alpha$ is obtained from Eq. (13) with $g_1 = t'_0$, $g_2 = v_1$. Since $t'_0 = t''_0$ and Γ_1 is about twice as large for ET when $\Delta = 0.5$ eV, the dissociation rate $1/\tau_1$ is about twice as large for ET as for HT and the τ_1 values $1/2$ as large.

In summary we have calculated the dissociation rate of an exciton on a donor or acceptor chain into a free electron on A and a free hole on D by a process that conserves energy, *i.e.*, no phonons are involved. Also, the process is applicable to chains that are sufficiently long that broadening of their molecular orbital levels is at least as large as the spacing of the unperturbed discrete levels.¹⁰ For dissociation to be possible in the absence of an electric field whichever chain the exciton is generated on, the midgap of D must lie above that of A by at least the exciton binding energy plus $1/2$ the absolute value of the difference in the energy gaps. For the difference in midgaps greater than this amount the rate of dissociation decreases rapidly. The difference in midgap energy levels of the pair CN-PPV:MEH-PPV is close to satisfying the condition for maximum transfer rate. The transfer rate falls off so rapidly as the distance between D and A increases that essentially transfer can take place only between neighbors separated by perhaps 4 to 6 Å perpendicular to the chain direction. For a CN-PPV:MEH-PPV pair separated by 4 Å we calculate a hole transfer time ~ 50 fs, the electron transfer time being shorter by a factor 2. As a consequence, since it has been demonstrated that there is phase separation of the two polymers on a scale of 10-100 nm,⁸ and the exciton hopping time in PPV has been estimated as 0.4 ps,¹⁹ the dissociation rate will likely be determined by the time it takes the exciton to diffuse to a location where the required donor or acceptor is within ~ 4 Å.

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FIGURES

FIG. 1. Schematic of the relations between band structures required for hole transfer (center and right columns) and electron transfer (center and left columns) with exciton created on chain 2. The dashed line across the three columns is the zero of the energy scale chosen to coincide with midgap on chain 2. Midgaps of the other two chains are indicated with dashed lines.

FIG. 2. Γ_α ($\alpha = 1, 2$) as a function of B , where $B = 0.063d^2$, d being the perpendicular distance between chains in Å. Hole transfer: solid curves; Electron transfer: dashed curves.

FIG. 3. (a): Γ_1 as a function of Δ for different values of B . (b): Γ_2 *vs.* Δ for different values of B .







